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Direct-on-filter analysis of crystalline silica using photoacoustic Fourier transform-infrared spectroscopy

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Abstract

Photoacoustic Fourier transform-infrared spectroscopy (PA-FT-IR) has been used to perform direct-on-filter (DOF) analysis of crystalline silica using laboratory-generated filter samples. With these samples, the silica particles were embedded in the stable three-dimensional matrix of the filter. In this preliminary study, it was demonstrated that the photoacoustic (PA) signals generated from direct-on-filter measurements were significantly higher than the corresponding signals for equivalent amounts of silica particles placed directly in the photoacoustic detector cup. Studies with Min-U-Sil-5 loaded onto 9 mm filter stubs indicated a limit of detection of less than 10 μg. Additionally, Teflon filters were demonstrated to be more suitable for these measurements than other types. The photoacoustic FT-IR approach seems to be feasible for further development to use with full-sized personal sampling filters. Published by Elsevier Science B.V.

Keywords: Photoacoustic spectroscopy; FT-IR; Crystalline silica; Personal exposure

1. Introduction

Photoacoustic Fourier transform-infrared spectroscopy (PA-FT-IR) has been increasingly utilized for the qualitative analysis of samples, because it requires minimal sample preparation and has the ability to analyze optically opaque samples [1,2]. Although initially PA-FT-IR spectroscopy was used for the analysis of gases, research during the 1970s yielded theories of photoacoustic (PA) signal generation for powders and solids [3,4]. Research on solids indicates that PA signal generation is the combined result of thermal and pressure contributions, with the pressure contribution dominating in substances of high porosity [5,6]. Additionally, only the contributions originating within the thermal diffusion length from the illuminated surface of a solid are detected. The thermal diffusion length in turn is proportional to the square root of thermal conductivity, and the inverse square root of the density, specific heat, wavenumber, and mirror scanning speed [7]. Studies with powders corroborated this theory demonstrating that substances with greater porosity produced greater PA-FT-IR signals than those substances with lower porosity [8]. Analysis of powders, however, has been fraught with variance because of the non-homogeneity of the packing and non-uniformity of the air spaces.

Investigation in our laboratory explored whether PA-FT-IR could be used for the direct-on-filter (DOF) analysis of crystalline silica for assessment of personal exposure. Typically, air in the work environment is pumped through a personal sampler mounted with a filter, 37 or 25 mm in diameter, to collect particles of sizes in the respirable range for silica exposure assess-

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ment [9]. The assessment of personal exposure to silica is important because of the continuing trend of preventable fatality, due to inhalation and subsequent deposition of crystalline silica in the lungs, of several hundred workers every year [10]. Additionally, crystalline silica in the inhaled form was recently classified as a known human carcinogen by the International Agency for Research on Cancer [11]. Current measurements of silica particles on personal exposure filters, acceptable to US regulatory agencies are laboratory methods based on either X-ray diffraction or infrared absorption with a diffraction grating spectrometer [9]. All these methods require sample preparation and can take as long as 2 weeks to receive the results. A DOF method would expedite analysis time, could reduce cost, and might even be usable as a field technique for on-site analysis. Studies for this paper focused on laboratory deposition of crystalline silica onto sampling filters and subsequent analysis with PA-FT-IR. Until our study, no DOF method for crystalline silica analysis using PA-FT-IR had been published.

2. Materials and methods

2.1. Particle deposition on filters

Min-U-Sil silica powders (size fractions 5, 10, 30, and 40 μm) were obtained from US Silica (Berkeley Springs, WV). The different size fractions of Min-U-Sil powders were not monodispersed but rather sieve-selected up to various defined particle sizes. Particle deposition on sampling filters was performed in one of the two ways. In the aerosol deposition method, Min-U-Sil-5 powders were aerosolized using a fluidized bed aerosol generator (Model 3400, TSI, St. Paul, MN) and sampled onto filter studs using a 10 mm nylon cyclone sampler (Part number 456243, MSA, Pittsburgh, PA) to simulate the typical air sampling situation. Two filter types: PVC (GLA 5000, 5 μm pore, Gelman, Ann Arbor, MI) and Teflon (Zefluor^{TM}, 2 μm pore, Gelman) were used. Both filters are tortuous pore membrane filters approximately 150 μm thick. They are extremely hydrophobic and stable at laboratory conditions. Filters were not desiccated, but rather equilibrated at room temperature for several hours before weighing. In the suspended particle deposition method, suspensions were made with various Min-U-Sil powders in isopropyl alcohol and deposited onto the filter. A mild suction was applied to the backside of the filter. The types of filters used with the suspensions were PVC (GLA 5000, 5 μm pore, Gelman, Ann Arbor, MI), Teflon (Zefluor^{TM}, 2 μm pore, Gelman), and silver membrane (5 μm pore, Osmonics, Minnetonka, MN). Suspended particle deposition, instead of aerosolization, was used to facilitate the loading of filters with particles of different sizes, to control the deposition better and reduce the level of hazard associated with the aerosolization of crystalline silica. Sample filters deposited with silica suspensions were then dried at room temperature and weighed. In both methods, all weighing was done with a Model C-35 microbalance from Cahn (Madison, WI). The amount of silica deposition was taken to be the mass difference before and after particle deposition.

2.2. Measurements

PA-FT-IR spectra were measured using a MTEC Photoacoustics (Ames, IA) Model 300 photoacoustic detector and a Perkin-Elmer (Norwalk, CT) Model Paragon 1000 FT-IR spectrometer. This photoacoustic detector is a standard attachment that can be inserted in the sample chamber of most commercial FT-IR spectrometers. A schematic diagram of such an attachment is shown in Fig. 1. The output of the microphone detector is connected to the existing signal processing electronics of the FT-IR spectrometer. Mid-infrared spectra were normalized with the carbon black refer-

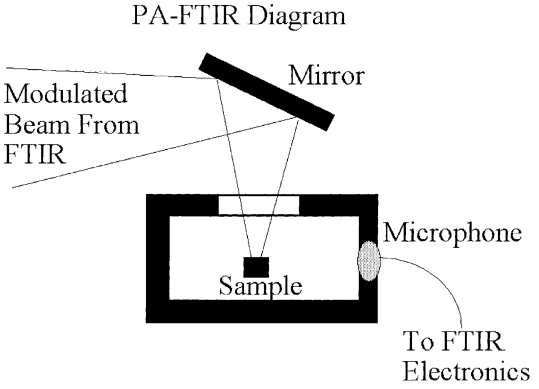

Fig. 1. Schematic diagram of the photoacoustic detector for commercial FT-IR spectrometers.

ence provided by MTEC Photoacoustics. Air served as the filling gas in the PA detector, and the FT-IR spectrometer was not purged. Since the sample cup in the PA detector is approximately 1 cm in diameter, 9 mm filter stubs were used for all filter measurements.

Series of spectra were averaged under identical conditions to improve signal-to-noise (S/N) ratios. Settings at spectral resolution of 4 cm^{-1}, scanning mirror speed of 0.1 cm s^{-1} and repetition number of 32 scans for the FT-IR spectrometer and a gain of two for the photoacoustic detector were used for the majority of measurements. In order to obtain the silica spectrum, each blank filter was used as its own reference for background removal, i.e. the PA spectrum of each blank filter was measured before particle deposition and then subtracted from the spectrum of the corresponding loaded filter. Peak heights of the silica spectrum were then measured against the baseline for subsequent analysis. Units for the PA signal are given in arbitrary units (a.u.) as presented by the instrument. Loaded filters with equivalent silica deposition but prepared by the two different methods were measured to confirm that similar results were obtained.

3. Results and discussion

Fig. 2 shows the relevant section of a FT-IR spectrum of crystalline silica displaying the doublet (800 and 780 cm^{-1}) which distinguishes quartz from the other polymorphs of silica—tridymite and cristobalite [12]. Although other quartz peaks could be used for infrared analysis, this doublet was chosen because of this identifying characteristic.

Initial work was done with generated aerosols of Min-U-Sil-5 silica loaded on PVC filters. Measurements were performed to determine the direct-on-filter sensitivity and to compare with the results of placing the silica powder directly in the sample cup of the photoacoustic detector. Using this DOF PA-FT-IR technique and the corrected peak heights at 800 cm^{-1}, the linear range for silica determination was up to approximately 80 μg. On the other hand, the linear range for placing silica particles directly in the sample cup extended to beyond 600 μg. Fig. 3a and b display the calibration curves for these two cases. The scales used in these two graphs are very different. The PA signals generated from crystalline silica embedded in a filter were significantly higher than the corresponding signals for equivalent amounts of silica particles placed directly in the sample cup. The limit of detection (LOD) for DOF analysis, defined as the signal just exceeding the signal of the blank filter by three standard deviations of the contribution from the blank filter [13], was found to be less than 10 μg. Since this DOF PA-FT-IR approach was nearly as sensitive as the recommended laboratory methods for the determination of crystalline silica, additional study was continued.

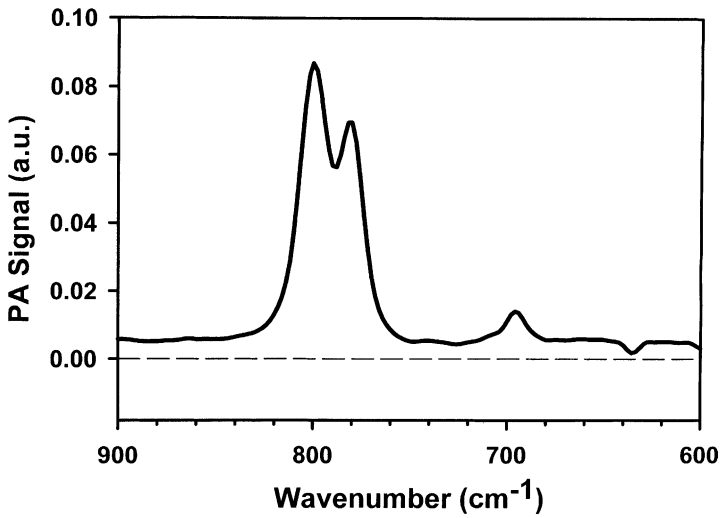

Fig. 2. Section of crystalline silica spectrum showing the identifying doublet.

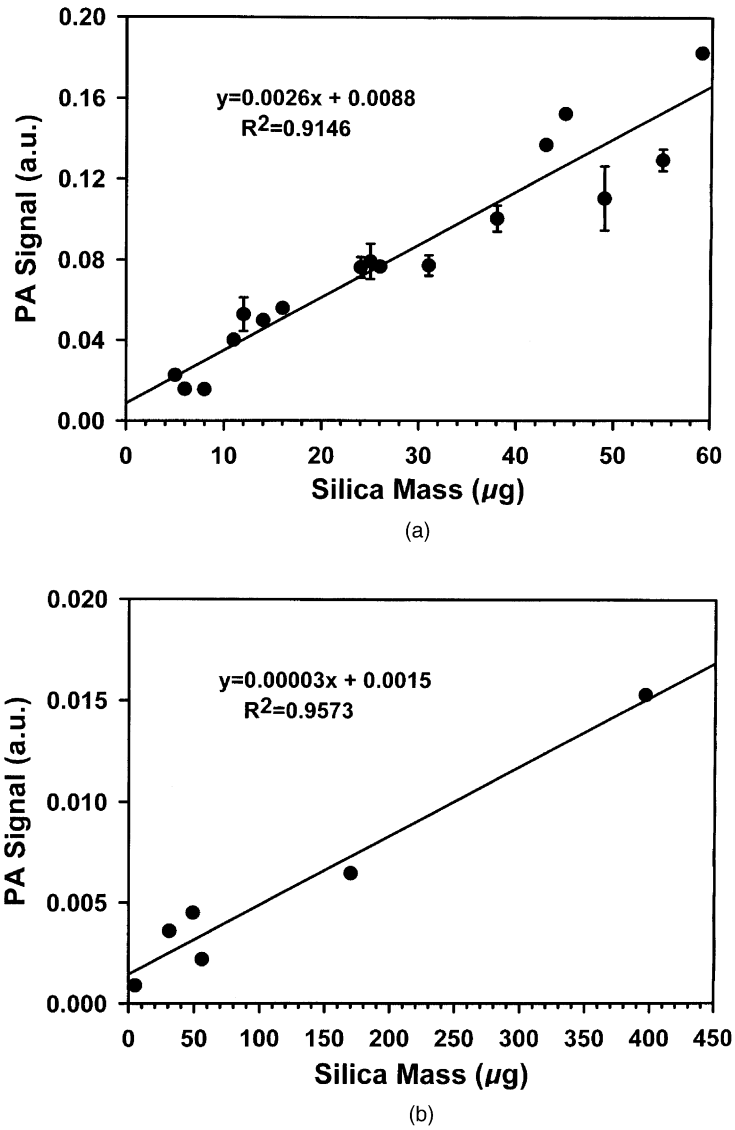

Fig. 3. PA-FT-IR calibration curves for deposition of Min-U-Sil-5 silica on (a) PVC filter, and (b) directly in the sample cup.

Saturation in the PA signal generation is an important issue. Above the saturating load level, the PA signal stayed more or less constant due to agglomeration of silica particles on the filter surface, instead of penetrating into the filter. Heavy particle loading led to the loss of interparticle air space reducing the pressure contribution of PA signal generation [5,6], and additionally any PA signal originating at a distance further than the thermal diffusion depth from the filter surface would be missed [7]. At high silica loading, less of the filter contribution was actually detected—this fact could lead to incorrect removal of the background PA signal due to the blank filter itself. When the PA-FT-IR spectrum for the blank filter was subtracted from the measured spectrum of the overloaded filter, negative values could be the result for spectral regions dominated by contributions due to the filter material. This phenomenon is demonstrated in Fig. 4

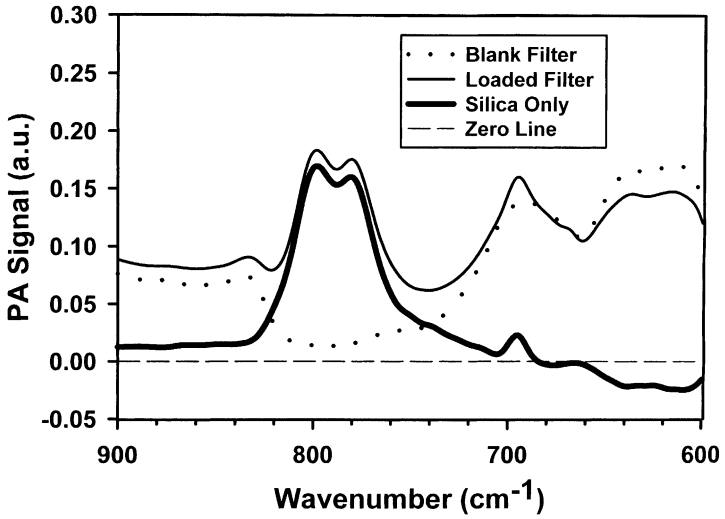

Fig. 4. PA-FT-IR spectra of blank filter, loaded filter, and silica only for 100 μg of Min-U-Sil-5 on a PVC filter.

which shows three spectra—blank filter, overloaded filter, and their difference representing silica only. The thick curve, representing silica only, is not exactly similar to the reference silica spectrum (Fig. 2) particularly in the spectral region 600–720 cm^{-1} where the PVC contribution dominates.

Since varying the mirror scanning speed of the FT-IR spectrometer would change the sampling depth, the effect on the generated PA signals was studied with different amounts of Min-U-Sil-5 silica loaded onto PVC filters, Fig. 5. The same loaded filters were used at increasing mirror scanning speeds. In principle, the mirror scanning speed controls the sampling depth and has been utilized in depth profiling studies [7]. Conventional theory holds that for homogeneous solids, the slowest mirror speed should yield the highest PA signals. However, for particles loaded onto the sampling filters, increasing the mirror scanning speed

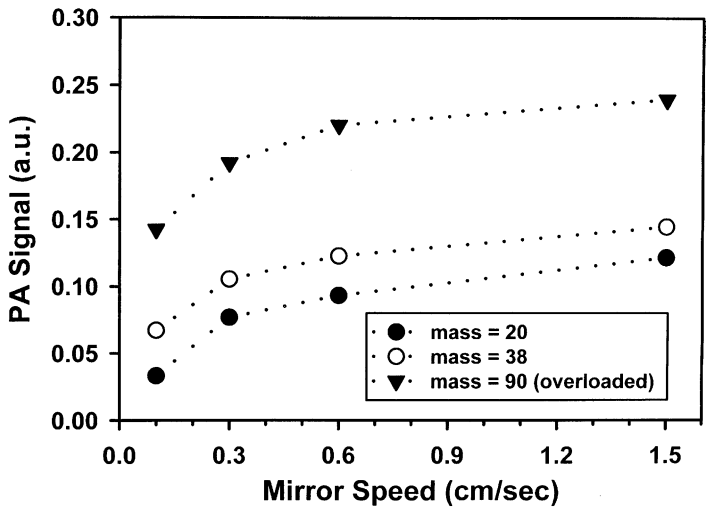

Fig. 5. Mirror scanning speed dependence of the PA-FT-IR signals for different masses of silica on PVC filters. The masses are given in μg.

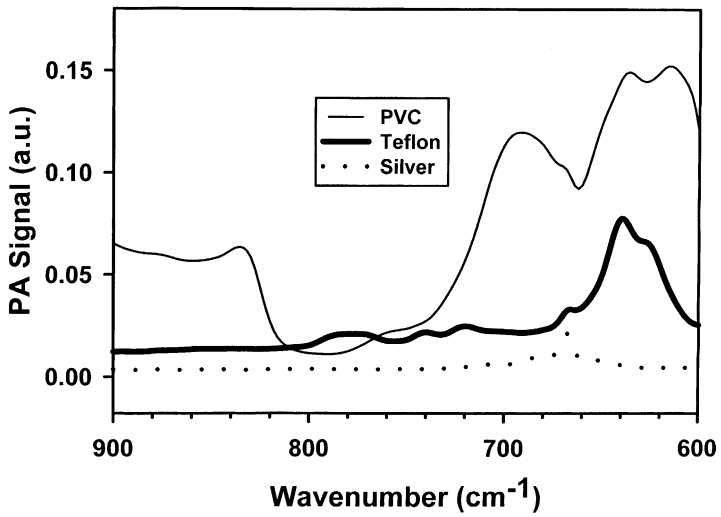

Fig. 6. PA-FT-IR spectra of three blank filters made of different materials.

was found to increase the PA-FT-IR signal until saturation. In addition, our results indicated that the variations of the PA signal versus scanning mirror speed were similar for filters loaded with silica particles in amounts within and beyond the linear measurement limit, i.e. 80 μg. The cause of the observed signal saturation at increasing scanning mirror speed should not be the reduced interparticle air space due to agglomeration of particles, but some so-far unexplained phenomena in PA signal measurement of particles loaded on filters.

Studies of particle size dependency were performed with sampling filters loaded with the four different size fractions of Min-U-Sil powders. Our results for particles deposited on a filter are in qualitative agreement with earlier and independently conducted research

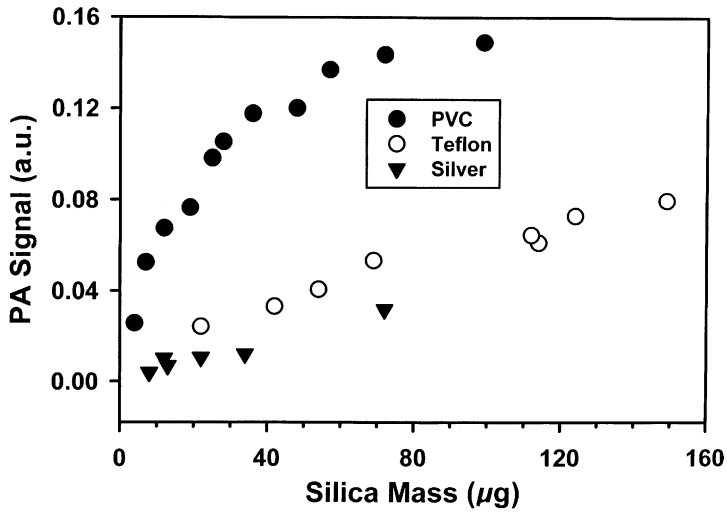

Fig. 7. PA-FT-IR calibration curves for deposition of Min-U-Sil-5 silica on different filters.

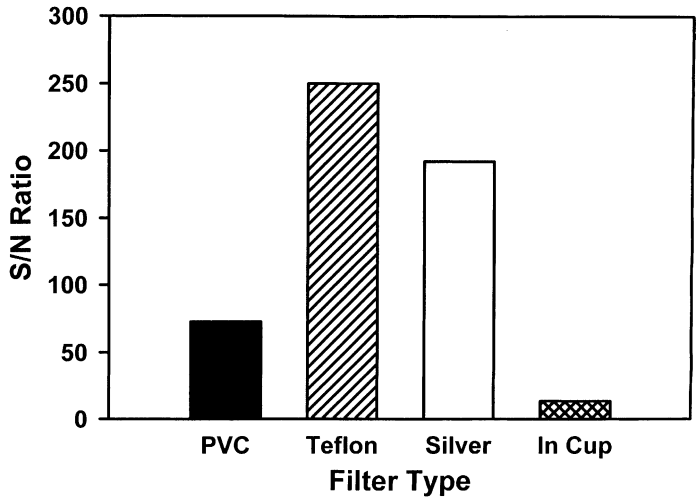

Fig. 8. Signal-to-noise (S/N) ratio of on-filter and in-cup measurements for 50 μg of Min-U-Sil-5 silica.

using particles of similar size fractions loaded directly in the sampling cup of the PA detector [8]. In general, the observed photoacoustic signal for silica particles of a smaller size fraction is higher than the corresponding signal for the same amount of silica particles of a larger size fraction.

Although a PVC filter is specified in the current sampling protocol for silica determination [9], filters made of a different material could potentially be more suitable when a different measurement technique is used. The suitability of various filter materials for DOF PA-FT-IR measurement was investigated to locate the filter types that contributed negligibly in the silica doublet region and at the same time yielded the best (S/N) ratio. Noise was defined as the standard deviation in the PA signal for the blank filters at the silica doublet region. Three different filter materials (PVC, Teflon, and silver) were identified, among those commercially available, to exhibit relatively low contributions photoacoustically in the region of the silica doublet, Fig. 6. Due to the differences in physical structures and thermal properties of the filters, the PA signals generated for a given amount of silica would not be the same. Although Min-U-Sil-5 loaded on PVC filters generated the highest PA signals, Fig. 7, Teflon filters yielded the greatest S/N ratio, Fig. 8. All three filters led to a S/N ratio higher than that of placing silica particles directly in the sample cup of the PA detector.

4. Conclusions

The results of this feasibility study indicate that PA-FT-IR spectroscopy may be a valid technique for DOF determination of crystalline silica. A linear relationship is found between the PA signal and the mass of crystalline silica loaded on the filter up to the point of saturation. This approach is more sensitive than measuring with particles directly in the PA detector cup. For silica loading over the saturation point, the measured spectra show artifacts in spectral regions dominated by contributions from the filter material.

Varying the scanning mirror speed of the FT-IR spectrometer led to a signal variation opposite to that expected from theory for homogeneous solids. Further studies by interested investigators might be worthwhile to understand the mechanism of photoacoustic signal generation for particles deposited onto tortuous pore membranes.

Signal variation trend obtained with the sieve-selected silica particles of different size fractions, deposited on filters, is in general agreement with an independent study using silica particles of corresponding size fractions, directly in the sample cup. A decreasing trend is indicated for the PA signal for larger particle size.

Among commercially available filter types, a Teflon filter is found to be the most suitable for DOF PA-FT-IR measurement of deposited crystalline silica.

This contrasts with DOF studies for transmission spectroscopy where Teflon and silver filters can not be used due to low transmission at the spectral region of interest. This highlights the importance of parameter revision upon modification of existing techniques.

Since the results of this preliminary study are obtained with silica particles deposited onto 9 mm filter stubs, comparison of performance with currently acceptable methods is not meaningful. However, this photoacoustic FT-IR approach seems to be feasible for further development. Future studies will focus on the analysis of full-sized (25, 37, and 47 mm) filters in a custom-designed PA detector, the investigation of spectral interference, and the determination of matrix effects.

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